

# PATENT SPECIFICATION

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## (54) PROCESS FOR PREPARING AQUEOUS ANTIMONY-III HALIDE SOLUTIONS

(71) We, HOECHST AKTIEN-GESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described and by the following statement:—

This invention relates to the preparation of acidic, aqueous antimony-III halide solutions from inactive antimony halide catalysts. Such inactive antimony catalysts are substantially composed of antimony (III) and antimony (V) halides, but also contain mineral and organic impurities. Antimony catalysts substantially composed of antimony pentachloride and antimonous chloride are used industrially for the preparation of fluorinated chlorohydrocarbons from chlorohydrocarbons in the liquid phase. Such processes are described, for example in German Patents Nos. 1,020,968 and 1,443,616.

The used catalyst solutions are partially liquid, partially solid and highly hygroscopic. Depending on the chlorohydrocarbon selected and the reaction time they contain up to about 40% of organic components as impurities, mainly derivatives of chlorofluoroethane, as well as solid hexachloroethane and rather small quantities of tarry products deposited at the bottom. They also contain small quantities of metal salts resulting from the material of the reaction vessel, especially iron and nickel halides. Antimony in the inactive catalysts is mainly present as antimony pentachloride, only about 1 to 10% of chlorine being replaced by fluoride.

For economical reasons it is desirable to work up the used catalyst and to recover the valuable antimony portions. Previously proposed processes for working up antimony-containing used catalysts have

not been used hitherto because of their complexity.

German Auslegeschrift No. 2,056,648 recommends heating the used catalyst with trichloroethylene to a temperature of from 100 to 170°C thus reducing pentavalent antimony to trivalent antimony, separating the antimonous chloride from the organic solution in a crystalline form and working it up to antimony pentachloride.

German Offenlegungsschrift No. 2,110,797 recommends heating the used catalyst to about 170°C while refluxing, benefiting from the thermal dissociation equilibrium of antimony pentachloride to antimonous trichloride and chlorine. Thus antimonous chloride is separated from the catalyst mixture in crystalline form. Both processes have the disadvantage that high reaction temperatures are required, and they bring about considerable problems involved with the material used.

According to British Patent No. 1,379,412 the used catalyst is mixed with a mineral acid or water, whereby the antimony halides are either dissolved or suspended in the aqueous phase, depending on the acid concentration, while the organic impurities precipitate for form a separate organic phase. Thereafter the antimony is precipitated as hydroxide or sulfide.

German Offenlegungsschrift No. 2,140,188 proposes a process which also involves treating the used catalysts with water. After separation of the organic phase antimony oxide is precipitated with ammonia in order to remove fluoride ions. The separated oxide is then dissolved in hydrochloric acid and treated with reducing agents. Antimonous chloride is finally obtained by distillation *in vacuo*. This process also necessitates several reaction steps.

For some purposes, anhydrous antimony halides are not used. For the preparation of chrome yellow or molybdate red, for example, aqueous antimony-containing

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solutions may be used as starting materials (German Patents Nos. 1,224,858 and 1,253,384).

5 The present invention seeks to provide an economic process for the preparation of aqueous antimony (III) halide solutions from inactive antimony halide catalysts containing substantially antimony (III) and antimony (V) halides besides mineral and  
10 organic impurities. This process can be carried out smoothly without using expensive auxiliary chemicals.

The present invention therefore provides a process for the preparation of an aqueous antimony (III) halide solution from an  
15 inactive antimony halide catalyst composed substantially of antimony (III) and antimony (V) halides, and organic and mineral impurities, which comprises mixing the inactive catalyst with a quantity of  
20 water or aqueous hydrochloric acid such that two liquid phase are formed, reducing antimony (V) to antimony (III) with sulfur dioxide, sulfite, pyrosulfite or antimony in pulverulent form in the aqueous phase and  
25 separating the organic phase from the aqueous phase prior to or after reduction.

The amount of acid or water added to the used catalyst for obtaining two separable  
30 phases depends on the antimony content of the catalyst and on the concentration of the acid used. When water is used, only a small quantity is required, whereas larger amounts of concentrated acid are needed; the use of water or aqueous hydrochloric  
35 acid having a hydrogen chloride content of up to 5% by weight is therefore preferred. The amount of water or acid may be simply determined by preliminary tests. The  
40 following amounts, for example, are required for the formation of two liquid phases, in dependence on the acid concentration when using catalysts having an antimony content of from 20 to 25%:  
45 about 15% by weight when using water, about 20% by weight when using 3N HCL, about 30% by weight when using 6N HCL, about 60% by weight when using 9N HCL and about 110% by weight when using 11N  
50 HCL, calculated on the catalyst.

The upper limit of the amount of water to be added is determined by the formation of antimony-containing precipitates which are insoluble in water. It is commonly known  
55 that hydrolysis yielding antimony hydroxychloride may occur when adding significant quantities of water to antimonous chloride. When using fairly dilute acids, for example 4N HCL, precipitates are not observed, even when  
60 diluted with larger quantities of water.

The distribution equilibrium of the antimony is mainly in favour of the aqueous phase during the extraction. Even when  
65 using the minimum quantity of water or

dilute acid there are always more than 99% of antimony in the aqueous phase. In this way solutions of relatively high concentration may be prepared having an antimony content of more than 30% by  
70 weight. In these cases the aqueous phase forms the more dense phase. When using highly contaminated catalysts it may sometimes be difficult to obtain an aqueous phase free from tarry impurities. In these  
75 cases it has proved advantageous to dilute the aqueous phase up to an antimony content of about 15% so that it forms the less dense phase. Even when diluting with water hydrolytic formation of antimony  
80 hydroxychloride cannot be observed.

The separation of the organic phase from the aqueous phase may be carried out prior to or after reduction. It is, however, advantageous to separate the organic phase  
85 after reduction, since the solubility of the organic phase in the aqueous phase is reduced by the reduction of  $Sb^{3+}$ .

The reduction with sulfur dioxide, bisulfite, pyrosulfite or metallic antimony powder may be performed at a temperature  
90 of from 10 to 110°C, preferably from 20 to 90°C. The reducing agent is generally used in a stoichiometric amount or in an excess of up to 50%. This applies especially to those cases where considerable quantities  
95 of fluorine are contained in the catalyst. The reduction may be performed in an especially good manner at a temperature of from 40 to 80°C. The use of antimony powder as reducing agent permits the  
100 preparation of solutions having  $Sb^{3+}$  contents of about 40% by weight. The reduction of antimony (V) in the process according to the present invention generally  
105 takes place smoothly when the inactive catalyst contains only from 0 to 10%, preferably from 0 to 2% by weight of fluorine. Higher quantities of fluorine, which might disturb the reduction, may be  
110 readily removed from the aqueous solution, by the addition of calcium chloride, in the form of insoluble calcium fluoride.

It is known that the reducing effect of sulfurous acid is hindered by organic  
115 compounds, whereas metal ions, especially manganese (II), iron (II) and copper (I) ions, and potassium bromide and potassium iodide accelerate the reduction. It is therefore advantageous to add, with sulfur  
120 dioxide, bisulfite or pyrosulfite, small quantities of these salts as redox catalysts.

Potassium iodide in an amount of 0.02%, or potassium bromide in an amount of 1%,  
125 calculated on the antimony, are generally sufficient. The reduction with bisulfite and sulfur dioxide may be performed without previous separation of the organic phase in the presence of these catalysts.

The antimonous chloride solution 130

obtained according to the present invention may be neutralized in known manner with ammonia, so that antimony trioxide is obtained. This solution is especially useful for the preparation of lead chromate pigments. These pigments include all those containing lead chromate as the main component. Besides the relatively pure lead chromates they also comprise mixed crystals containing lead sulfate or lead molybdate or both, as additional components. The following lead chromate pigments may be mentioned, by way of example: Chrome Yellow CI-77600, Basic Lead Chromate CI-77601, Lead Sulfochromate CI-77603, Molybdate Orange or Red CI-77605 (Color Index, 2nd edition, 1956).

The process according to the present invention consequently enables a cumbersome waste product to be worked up to such a degree that it may be used for the preparation of pigments. It is surprising that the aqueous solutions obtained according to the present invention which contain besides antimony (III) chloride, generally  $\text{Fe}^{3+}$  and sulfate ions, allow the preparation of perfect lead chromate pigments.

The following Examples illustrate the invention:

#### EXAMPLE 1:

680 g of 4N hydrochloric acid are added to 3000 g of inactive catalyst (containing 2% of F, 30% of CL, 18% of  $\text{Sb}^{3+}$ ) while stirring and cooling. Thereafter 2200 g of hydrochloric acid phase are separated containing 29.1% of Sb, which corresponds to 97% of initial quantity of antimony. This phase is halved. 680 g of 40% sodium bisulfite solution are added dropwise, while stirring, to 1100 g of the hydrochloric acid phase, and the reaction temperature rises to 60°C.

The  $\text{SbCl}_3$  solution obtained after cooling and filtering off small quantities of organic components has a ratio of  $\text{Sb}^{3+}:\text{Sb}$  (total quantity) (=degree of reduction) of 0.96.

#### EXAMPLE 2:

The second half of the hydrochloric acid phase obtained in Example 1 is diluted with 260 g of 4N HCL and mixed while stirring with 212 g of Sb powder (corresponding to 120% of the stoichiometric amount). The temperature rises to 80°C, and the whole amount of antimony is dissolved. The solution obtained after filtration of solid impurities has a degree of reduction of 0.98%.

#### EXAMPLE 3:

1000 g of used catalyst are mixed while

stirring with 500 g of 3N hydrochloric acid. The catalyst used has the following composition: 22% of  $\text{Sb}^{3+}$ , 3% of  $\text{Sb}^{5+}$ , 1% of fluoride, 0.5% of  $\text{Fe}^{3+}$ , 0.1% of arsenic, 8.6% of F 112; 4.5% of F 21; 7.4% of F 111; 5.0% of F 122; 2.6% of tetrachloroethane, 2.3% of pentachloroethane and 2.3% of hexachloroethane.

The hydrochloric acid mixture is mixed with 5 g of potassium bromide and sulfur dioxide is introduced while stirring, until no more  $\text{SO}_2$  is absorbed. The reaction temperature rises to 40°C. The mixture is cooled to 20°C and 1150 g of aqueous phase are separated. This phase contains 172 g of sulfate, 246 g of  $\text{Sb}^{3+}$ , 2g of  $\text{Sb}^{5+}$ , 5g of  $\text{Fe}^{3+}$ , 10 g of fluoride and 3.3 g of bromide.

#### EXAMPLE 4:

500 g of water are added while stirring and cooling to 1000 g of used catalyst (composed of 22% of  $\text{Sb}^{3+}$  and 3% of  $\text{Sb}^{5+}$ ). About 0.1 g of KI is added to the mixture and  $\text{SO}_2$  is introduced in the manner described in Example 3, until no more  $\text{SO}_2$  is absorbed. The ratio of  $\text{Sb}^{3+}:\text{Sb}$  (total quantity) in the hydrochloric phase is 99%.

#### EXAMPLE 5:

The process of Example 2 of German Patent No. 1,253,384 is repeated. A pigment of the same resistance to  $\text{SO}_2$  and of the same tone was obtained when using, instead of a solution of 20 g of antimony (III) chloride in 40 ml of water, 49.5 g of the solution obtained in Example 3 above.

#### WHAT WE CLAIM IS:—

1. A process for the preparation of an aqueous antimony (III) halide solution from an inactive antimony halide catalyst substantially composed of antimony (III) and antimony (V) halides or organic and mineral impurities, which comprises adding a quantity of water or aqueous hydrochloric acid to the inactive catalyst such that two liquid phases are formed, reducing antimony (V) to antimony (III) with sulfur dioxide, sulfite, pyrosulfite or antimony in pulverulent form in the aqueous phase and separating the organic phase from the aqueous phase prior to or after the reduction.

2. A process as claimed in claim 1, wherein the quantity of water or hydrochloric acid is such that the aqueous phase forms the less dense phase.

3. A process as claimed in claim 1 or claim 2, wherein the organic phase is separated from the aqueous phase after the reduction.

4. A process as claimed in any one of claims 1 to 3, wherein there is added to the inactive antimony halide catalyst water or

aqueous hydrochloric acid having a hydrogen chloride content of up to 5% by weight.

5 5. A process as claimed in any one of claims 1 to 4, wherein reduction is carried out with sulfur dioxide, sulfite or pyrosulfite in the presence of a redox catalyst.

10 6. A process as claimed in any one of claims 1 to 5, wherein the antimony halide catalyst contains from 0 to 2% by weight of fluorine.

7. A process as claimed in claim 1 carried out substantially as described in any one of Examples 1, 2, 3 and 4 herein.

8. An aqueous antimony (III) halide solution whenever prepared by a process as claimed in any one of claims 1 to 7.

9. A lead chromate pigment which has been prepared in the presence of a solution as claimed in claim 8. 20<sup>2</sup>

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